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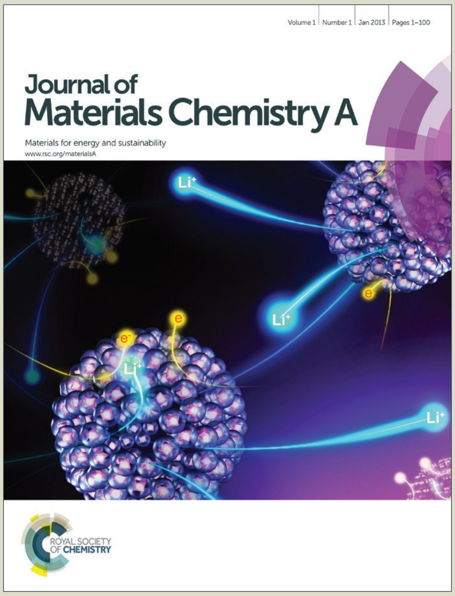

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Surface Functionalization of Conjugated Microporous Polymer Thin Films and Nanomembranes using Orthogonal Chemistries

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Conjugated microporous polymers (CMP) have attracted large interest due to their intrinsic porosity, outstanding stability and high variability. Here we present the surface modification of CMP thin films and nanomembranes *via* orthogonal chemistry. Using the light induced thiol-yne reaction for the functinoalization provides the additional opportunity to photo-pattern the CMP materials.

Modification and functionalization of surfaces and control over interface properties has become increasingly important due to miniaturization of active devices and the resulting increase in surface to volume ratios[1]. Recently, conjugated microporous polymers (CMP) have attracted wide interest due to their low densities, large surface areas and the possibility to incorporate different kinds of functional groups in a modular fashion.[2] [3] Since CMP materials are prepared from irreversible reactions, they are usually amorphous, but at the same time often show narrow pore size distributions.[4] [5] The resulting materials show exceptional thermal and chemical stability, which goes well beyond that of related metal organic frameworks (MOFs)[6] and covalent organic frameworks (COFs)[7] making this class of microporous materials particularly appealing for practical applications, such as gas storage, catalysis and molecular separation.[8] In order to optimize their performance, next to the material composition, also their controlled synthesis as thin films plays a crucial role. Gu et al. have developed an electrochemical route to prepare CMP films [9]. Subsequently this strategy has been followed to apply CMP materials for application in sensing [10], photoenergy conversion [11] and as electrode materials in supercapacitors [12]. In addition Becker at al. have introduced a direct synthesis of CMP on gold electrodes using a self-assembled manolayer (SAM) as anchor group [13]. We recently introduced a layer-by-layer (LbL) method for their controlled synthesis on surfaces and, by using sacrificial substrates[14], as freestanding CMP-nanomembranes with thicknesses as low as few nanometers[15]. In order to further adapt the membrane features to the desired applications[16], in addition to tuning the pore-size distribution and the internal structure of the nanomembranes, also an adjustment of their surface properties, in particular their wetting behavior, is of crucial importance to optimize the interaction between the membrane and the target molecules. Due to the exceptionally high surface to volume ration of such thin films and nanomembranes, the control over their surface properties are particularly important.

In this work we present a novel strategy for the post-synthesis functionalization of the external surface of CMP nanomembranes. The approach is based on two types of click chemistries, which are orthogonal to each other [17], the copper(I)-catalyzed alkyne-azide cycloaddition (CuAAC) [18] and the light induced thiol-yne reaction[19].

The CuAAC reaction is used for the preparation of the CMP nanomembranes *via* a LbL approach. In the last layer a building block with alkyne functional groups was used. The surface alkyne moieties are then used in the thiol-yne reaction. This reaction scheme is fast, has no by-products and in particular, the method allows for a straightforward photopatterning of the membrane surface.[20] Prior to the light-induced surface functionalization the CMP-membranes were transferred to a gold-wafer *via* a previously described transfer process.[15] The reaction scheme for the outer surface modification as well as a schematic representation is shown in **Figure 1**.

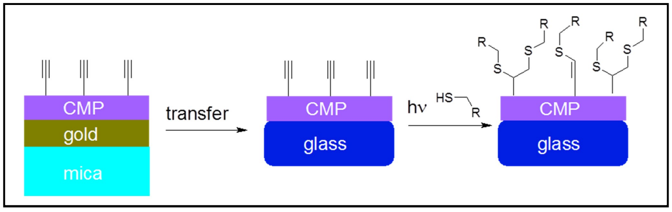

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Figure 1. Surface modification of CMP-nanomembranes using photo-induced thiol-yne click chemistry. The transfer to a glass substrate is shown as an example. The CMP-membrane on glass is necessary for the fluorescence experiments.

To illustrate the potential of this approach, we choose three different molecules for the surface functionalization to control the wettability of the CMP nanomembranes. To get a hydrophobic surface we used 1H,1H,2H,2H-perfluorodecanethiol as coupling agent. Cysteamine and 3-mercaptopropionic acid, on the other hand, resulted in hydrophilic outer surfaces.

After the corresponding light-induced surface thiol-yne reactions the modified CMP-membranes were characterized with IRRA-spectroscopy (see **Figure 2**).

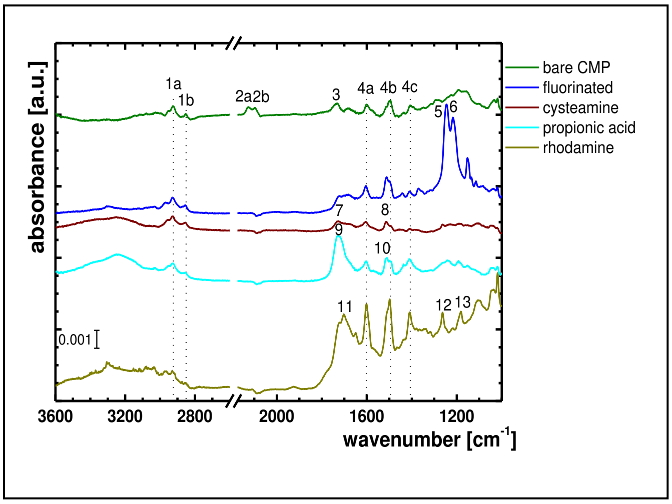

Figure 2. IRRA-spectra of CMP-nanomembranes before and after surface modification using photo-induced thiol-yne click reaction using the following thiols. Green: bare membrane without functionalization; Blue: HS-$(CH_2)_2$-$(CF_2)_7$-CF_3; Dark red: HS-$(CH_2)_2$-NH_2; Cyan: HS-$(CH_2)_2$-COOH; Dark yellow: HS-rhodamine.

In comparison to the bare CMP-membrane, the CMP-membranes after reaction show the same bands for the aromatic backbone, i.e. the internal structure of the membrane is not influenced by the reaction. In addition to the membrane signals, the characteristic bands for the introduced functional groups could be clearly observed (for a detailed list of the functional groups and the corresponding band positions see **Table 1**).

No.	Band (cm^{-1})	vibration/functional group	modification
1a/b	2925/2852	ν_{as}/ν_s CH_2	bare CMP
2a/b	2126/2098	ν alkyne; ν –N_3	bare CMP
3	1729		bare CMP
4a/b/c	1603/1495/1407	vibration of aromatic backbone	bare CMP
5	1248	ν CF_3	CF_3
6	1219	ν CF	CF_3
7	1727		NH_2
8	1515	δ NH_3^+	NH_2
9	1729	ν C=O	COOH
10	1512	ν =C-H and ring C=C	COOH
11	1702	ν C=O	rhodamine
12	1263	δ =C-H aromatic	rhodamine
13	1181	ν CN	rhodamine

Table 1: Assignment of the bands in the IRRA-spectra shown in Figure 2.

To investigate the influence of the surface functionalization on the wetting properties of the CMP-nanomembranes, we measured the water contact angle before and after the reaction. The corresponding images are shown in **Figure 3**. Prior to surface functionalization the alkyne-terminated CMP-membrane is weakly hydrophilic (54° ± 5°). This contact angle decrease slightly, by ≈12°, after reaction with the 3-mercaptopropionic acid (42° ± 2°). The change in hydrophilicity is substantially more pronounced in case of cysteamine, where a reduction of the contact angle down to 34° ± 7° is seen. Normally the COOH-terminated surfaces of high quality SAMs show lower contact angles.[21] However in our case the higher contact angles can be explained by intermolecular hydrogen bonds.[22] As expected, the fluorinated surface prepared by grafting the perfluorodecanethiol to the surfaces yielded a strong increase in contact angle to 104° ± 8°.

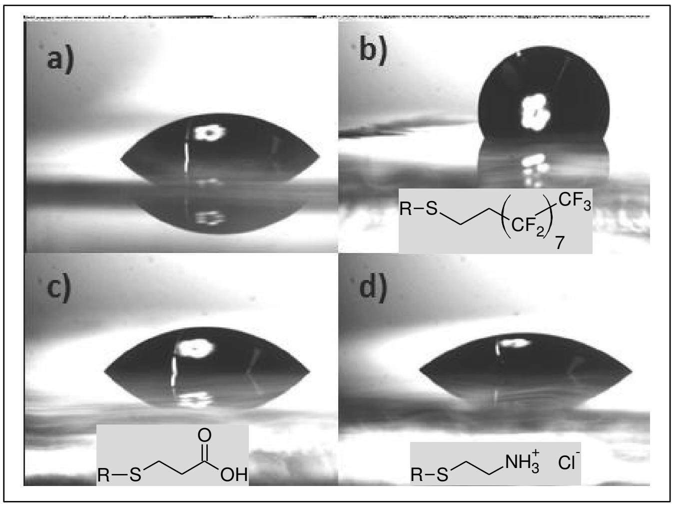

Figure 3. Water contact angle images of CMP nanomembranes: a) before modification; b) hydrophobic modification with HS-$(CH_2)_2(CF_2)_7$-CF_3; c) hydrophilic modification with HS-$(CH_2)_2$-COOH and d) hydrophilic modification with HS-$(CH_2)_2$-NH_2 • HCl

As mentioned above, the photo-induced thiol-yne reaction provides the possibility to pattern the membranes by employing photo-masks.[20] In order to demonstrate the straightforward application of this approach we used a fluorescent dye (rhodamine-SH) containing a thiol group and irradiated the sample through a honeycomb pattern photo mask. After the reaction we rinsed the sample thoroughly with ethanol.

The fluorescence microscope images in **Figure 4** recorded after transfer of the functionalized CMP-nanomembranes clearly show the honeycomb pattern of the photo mask with high contrast. Only the irradiated areas appear bright, in the other regions a strongly reduced fluorescence is observed which results from the unspecific adsorption of the dye on the non-irradiated areas.

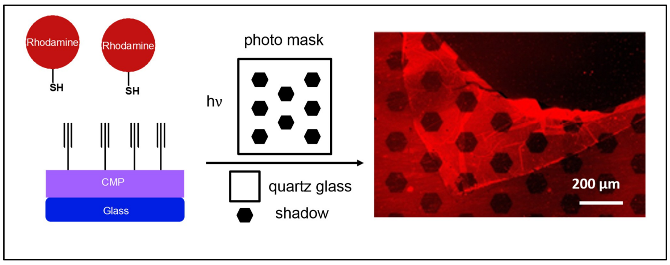

Figure 4. Scheme for the surface modification of the CMP-film by light induced thiol-yne reaction. The sample was irradiated through a photo mask. In the fluorescence microscope image on the right only irradiated parts of the CMP-membrane are showing strong red fluorescence.

After thorough rinsing of the samples, no change in the images could be observed, thus demonstrating that the surface modification *via* thiol-yne reaction leads to the formation of strong chemical bonds to the surface and allows ruling out that the surface modification results from weak physisorption of the dyes to the surface. To be sure that no UV-light induced reaction within the CMP-membrane is responsible for the fluorescence, the experiment was repeated without the dye. The honeycomb pattern was not observable in this case.

Conclusions

In conclusion, we have described a novel method to functionalize the outer surface of freestanding CMP-nanomembranes *via* thiol-yne reaction. Particular advantages of this new approach are the use of orthogonal chemistries and the possibility to photo-pattern the surface with appropriately functionalized molecules. Contact angle measurements demonstrated that the wettability of the membranes could be tuned in a predictable, straightforward fashion, thus strongly improving the potential of the CMP-materials for membrane applications.[16] The extension of this approach to the grafting of biomolecules to the membrane's outer surfaces will be straightforward.[23] In addition, the presented (patterned) surface functionalization method will also be of interest for applications of CMP materials in other fields, such as catalysis, sensing, or optics/electronics[24] [25] [26] [27].

Notes and references

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